MECHANISTIC INVESTIGATIONS OF THE IRON-SULFUR CATALYZED REDUCTION OF HYDROXYL-CONTAINING MODEL COMPOUNDS.

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INTRODUCTION.

The goal of our research has been to focus on the mechanisms of hydrogen transfer from donor solvents to coal model compounds in the presence and absence of iron/sulfur (FeS) catalysts. Previous work showed that hydrogen transfer from dihydroaromatic donor solvents occurs predominately by reverse radical disproportionation (RRD) and by free hydrogen atoms (HA) generated from the solvent derived cyclohexadienyl radicals.[1-6] Initially, our catalytic studies examined the efficiency of strong bond scission using a variety of FeS catalyst precursors.[7-9] Those studies showed that 6-line ferrihydrite (FeOOH) is an efficient precursor to highly active catalysts. A hydrogen donor solvent, 9,10-dihydrophenanthrene, promoted facile scission of strong carbon-carbon bonds ($Ar\text{-}CH_2Ar$) in those studies. Recent mechanistic studies have used structure reactivity arguments to show that hydrogen transfer from the FeS catalysts is consistent with selective and reversible hydrogen atom transfer from the reduced catalyst by a radical-like mechanism.[10-11]

In the present work we report our most recent results regarding the mechanistic pathways of hydrogen transfer from FeS catalysts to coal model compounds. The present study examines the effect of hydroxylic groups in the catalytic hydroliquefaction of coal. We report the results of our investigations of three different types of model compound structures, (1) *arylmethanols*; benzylalcohol, diphenylmethanol, 1-naphthalenemethanol, 1,2-diphenyl ethanol and (2) *alkyl alcohols*; 2-phenethylalcohol and octadecanol (3) *aryl alcohols*; phenol, naphthol and anisole. We show that reduction of these model compounds, by an apparent ionic pathway, competes with hydrogen transfer to the ipso-position of the substituted arenes.

EXPERIMENTAL.

Materials. All catalytic experiments used 6-line ferrihydrite, prepared by the Rapid Thermal Decomposition of Precursors (RTDS), as the catalyst precursor.[7] The 9,10-dihydrophenanthrene (DHP), 1 and 2-naphthol, phenol, 1-naphthalenemethanol, benzyl alcohol, 2-phenethyl alcohol, and octadecanol were used as purchased from Aldrich except for DHP. The DHP was distilled and recrystallized from methanol/dichloromethane. The 1,2-ditolylethanol was available from a previous study.[13]

Thermolysis Studies. Model compound (15 mg), 6-line ferrihydrite (3 mg), sulfur (3 mg), and DHP solvent (100 mg) were loaded into 5-mm o.d. borosilicate glass tubes and sealed under vacuum. Thermolysis was carried out in a fluidized sand bath regulated at the specified temperature for various times. The GC and GC/MS analyses of the products were carried out as described previously.[7]

RESULTS AND DISCUSSION.

Aryl Methanols. Thermolysis of benzyl alcohol at 270 °C in DHP containing 6-line ferrihydrite and sulfur produced toluene as the major observable product. However, the mass balance was less than 50% (Table I). Some higher molecular weight products, assigned by GC/MS analysis as benzylated phenanthrenes, were also observed, suggesting an ionic intermediate. Since benzyl alcohols readily undergo dehydration in the presence of trace amounts of acid to yield a cationic intermediate, it is reasonable to assume that the catalyst protonates the alcohol to generate a benzyl cation. Subsequent addition of the benzyl cation to the solvent, phenanthrene, is likely to provide the major pathway under the conditions used (Scheme I). This mechanistic scheme is consistent with the low mass balance observed for the catalytic reduction of benzyl alcohol.

Similarly, thermolysis of 1-naphthalenemethanol at 265°C for 60 minutes yielded 1-methylnaphthalene as the major product. Again, the mass balance for products detected by GC was low, 40-60%, based upon consumption of the starting material. Consequently it appears that the initial catalytic reduction of aryl methanols leads to retrogressive reaction products. However, at a higher temperatures of 325°C, the observed mass balance improved to 70% for the same reaction time. We believe this is a result of secondary catalytic thermolysis pathways, a reasonable assumption since we have shown that benzylated arenes are efficiently consumed in the presence of the FeS catalyst.[7]

Alkyl Alcohols. Thermolysis of 2-phenethyl alcohol led to the eventual formation of ethylbenzene (Table I). However, we observed the transient formation of phenethylthiol. The thiol concentration grew slowly during the reaction and subsequently decreased after long reaction times. This observation is consistent with dehydration of the alcohol to form styrene, an intermediate product leading to sulfur incorporation or reduction to ethylbenzene. It is reasonable to assume that the thiol is also converted to the styrene and H_2S by a similar mechanism (Scheme II).

Thermolysis of octadecanol yielded similar results. The concentration of octadecathiol was observed to grow in over a period of ca. 30 minutes and then to disappear. Analogous to the catalytic thermolysis of phenethylalcohol, aliphatic alcohols are reduced in the presence of the

catalyst.

Catalytic reduction of the methyl ester of 1,2-diphenylethanol yielded bibenzyl as the major product. This is noteworthy because if electron transfer from the arene to the catalyst were an important pathway, carbon-carbon bond scission of the 1,2-diphenylethanol radical cation is expected to yield toluene derived products.[14]

Aryl Alcohols. Thermolysis of 1- and 2-naphthol in DHP in the presence of the FeS catalyst precursor led to the formation of two major products, naphthalene and tetralin (Table I). After 60 minutes at temperatures between 320 - 330 °C, about 30% of the naphthol was consumed to yield roughly a 1 to 1.1 ratio of naphthalene to tetralin. For comparison, note that the thermolysis of phenol, even at higher temperatures (390 °C) yielded no observable chemistry. This is an interesting observation, given that in a control experiment, anisole, the methyl ether of phenol, was consumed at a comparable rate to naphthol, to yield phenol.

The observations of this study are consistent with our previously proposed mechanism involving reversible hydrogen atom transfer from the catalyst to the arene.[10] Ipso addition of a hydrogen atom is more endothermic than non-ipso addition and therefore not apt to be observed. The hydroxy group on naphthol stabilizes the radical adduct formed by transfer of a hydrogen from the catalyst. Hydrogen atoms likely transfer back and forth between the catalyst and the arene. Eventually the adduct is reduced by the transfer of a second hydrogen atom to yield dihydronaphthol. Subsequent reduction of the diene yields hydroxytetralin, followed by dehydration to dihydronaphthalene. Thermal pathways may also contribute to the observed products. (Scheme III).

As expected from our mechanistic proposal, aryl alcohols are reduced at a slower rate than either the alkyl or benzyl alcohols examined in this present work. Acid catalyzed reduction of aryl alcohols is expected to be extremely slow. Reduction of naphthol by a sequence of hydrogen atom transfer steps to yield an alkynol is the major route for the deoxygenation of 1 and 2-naphthol.

CONCLUSION.

Several pathways for the deoxygenation of the hydroxylic functional groups in model compounds are likely operating under iron/sulfur catalytic conditions. The initial step appears to be catalytic dehydration. Unfortunately, dehydration products may yield retrogressive reaction products. Catalytic dehydration of aliphatic alcohols yields intermediate olefins which incorporates sulfur under the reaction conditions. Reactions of benzylic alcohols leads to formation of benzylated solvent products. Fortunately, the formation of the thiol is reversible with the intermediate olefin being reduced to the corresponding hydrocarbon and the strong carbon-carbon bonds of benzylated arenes are efficiently cleaved in the presence of FeS catalysts in DHP. In summary: although the hydroxylic function in our model compounds are consumed at a rapid rate, they lead to products that must be 'treated' by further reactions with the catalyst to yield the desired products. The net result is a slight increase in hydrogen demand to bring about liquefaction of hydroxylated structures in coal model compounds.
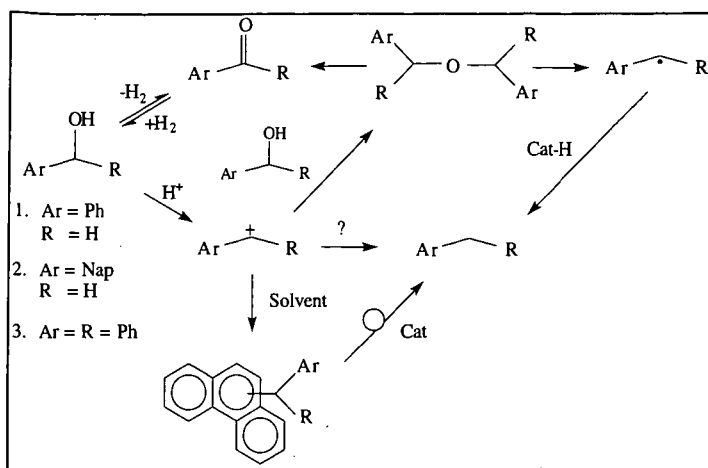
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Table I
Reaction Rates and Products of Model Compounds with "Iron-Sulfide" (FeS)
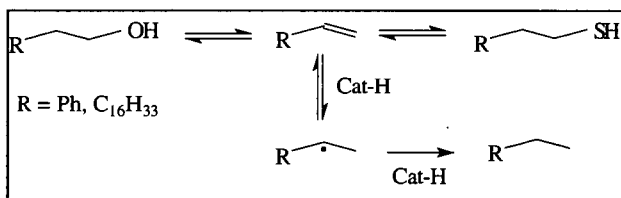Catalysts in Sealed Tube Reactions with 9,10-Dihydrophenanthrene

Model Compound	Reaction Temp. (°C)	Mass Balance	Disappearance Rate (x 10^{-4} s^{-1})	Major Products
Benzyl Alcohol	270	40-50%[a]	33 ± 4	Toluene[b]
1-Naphthalene Methanol	265	40-60%[c]	80 ± 10	Naphthaldehyde 1-Methylnaphthalene
2-Phenethyl Alcohol	315	80%	$4.7 \pm .6$	Ethyl Benzene[d]
Octadecanol	340	60-70%	5 ± 1	Octadecane[e]
Phenol	390	95%	No Reaction	None
1-Naphthol	320	90%	$0.7 \pm .1$	Naphthalene, Tetralin[f]
2-Naphthol	330	95%	$1.1 \pm .1$	Naphthalene, Tetralin[f]

a) Slightly higher mass balance was obtained for reactions at higher temperatures. b) Other products identified were benzaldehyde, and various isomers of benzylphenanthrene. c) Again higher mass balance was obtained for reactions at higher temperatures. d) Phenylethylthiol was identified by GC/MS. e) Octadecathiol identified by GC/MS. f) Close to a 1:1 ratio of the two major products was obtained.

Scheme I

-H₂ / +H₂ relationships shown.

1. Ar = Ph
   R = H

2. Ar = Nap
   R = H

3. Ar = R = Ph

$-H_2$ / $+H_2$

H^+

Cat-H

?

Solvent

Cat

Scheme II

R = Ph, $C_{16}H_{33}$

Cat-H

Cat-H

Scheme III

Cat-H

Cat-H

Cat-H

H_2O

H_2O

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